

1932

The effect of an electric field on the production of carbon black

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14

THE EFFECT OF AN ELECTRIC FIELD
ON THE PRODUCTION OF CARBON BLACK

BY

Oral A. Brown

A Thesis Submitted to the Graduate Faculty
for the Degree

DOCTOR OF PHILOSOPHY

Major Subject Electrical Engineering

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1932

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INTRODUCTION

The first carbon black manufactured as a commercial product from natural gas was made at a plant at New Cumberland West Virginia in 1872 (2). Since that time carbon black has found an ever increasing number of uses. More than 200 million pounds of carbon black are produced yearly in the United States (17).

Present methods of manufacturing carbon black produce different qualities of product. How to obtain these carbon blacks with different qualities is better understood than why different carbon blacks have different qualities. The variation in quality has been thought due to different temperature conditions. That temperature alone does not account for the differences has been shown by experiments with cooled metal surfaces (22). The variation, therefore, must involve other factors than temperature.

Jakosky (21) of the U. S. Bureau of mines used an electric field in an attempt to separate the carbon particles from the flame as quickly as possible. His idea was to get the carbon particle out of the flame before it hardened. The results were not satisfactory because as he says, "the current blew the flame out." Had he carried the experiment further he would

have found that the point at which the flame was blown out would have been the point at which no carbon was produced.

What happens when a hydro-carbon gas burns in air is a difficult question. Why some of the carbon atoms find oxygen atoms and unite with them to form CO_2 and others are deposited as a form of carbon which we call carbon black has been a question much discussed (23). The relation, however, that the actual chemical reaction which is called combustion has to the ionization of the surrounding gas is not understood (24). The relation that this ionization has to the formed carbon particles both as to quality and quantity has been completely overlooked.

The decreasing quantity of natural gas in the United States, together with the increasing amount of carbon black used, increasing lengths of pipe lines, and the low efficiencies of existing plants are strong arguments for more intense study of the factors involved in the production of carbon black.

Some experimental work in flame investigation led to the belief that there exists some relation between the amount of carbon black produced and the strength of the electric field in which the flame burns (26). Investigations have been carried on to determine if there are differences in the amounts of carbon black produced from a given amount of gas but with different electric fields and if there are any differences in tinting strengths, or iodine adsorptions for carbon black made in electric fields of different strengths.

HISTORICAL REVIEW

Factors influencing carbon black production.

The factors which might influence carbon black production are listed by Chamberlin and Rose (4) as follows:

- | | |
|----------------------------------|---|
| 1. Pressure of gas | 8. Motion of plate |
| 2. Rate of burning | 9. Shape of plate |
| 3. Nature of tip | 10. Humidity of atmosphere |
| 4. Composition of gas | 11. Barometric pressure |
| 5. Position of plate
in flame | 12. Temperature of gas |
| 6. Draft condition | 13. Temperature of plate |
| 7. Material of plate | 14. Uniformity of operating
conditions |

In their investigations they used an asbestos box built in the shape of a 1 foot cube. It was found that all the factors listed above did not affect quantity or quality.

In the discussion of the paper Mr. Chamberlin states, "We find that when the house is raised to 400° Centigrade, definite catalytic effects take place when the flame impinges on the plate. It gives carbon blacker in color, possibly some carbons which are lighter in color and gives higher or lower yield depending upon the conditions."

In their studies the maximum amount of carbon obtained

per 1000 cubic feet of natural gas was 2.17 pounds.

In a paper delivered before the same society Hill and Rhodes (9) stated, "One thousand feet of natural gas contains about 35 pounds of carbon, but only about one pound to one pound and a half is recovered by the usual process. The inefficiency, if considered solely from the gas standpoint, is rather appalling, and for this reason the manufacture of carbon black by the Channel process is looked upon with disfavor by intelligent natural gas men."

The impingement process for producing carbon black continues to be the most satisfactory one for producing the kind of carbon black needed. Wiegand (19) gives the following suggestions as to why this is true.

"Early Fixation. By quick removal of the carbon particles from the flame there tends to be less opportunity for growth or accretion, thus resulting in finer particle size.

"Electrical Repulsion. The luminous carbon particles emit electrons, and as a result are positively charged. This will tend to keep them apart up to the point of collection.

"Gaseous Adsorption. The luminous particles of carbon are in an active condition due to the heat released by their own combustion and also to that developed in the regions of gaseous combustion. They are bathed in carbon monoxide, carbon dioxide, hydrogen, nitrogen as well as some oxygen. As a result they carry with them, to the collecting plate or chan-

nel, an adsorbed layer of gases which is known profoundly to affect their properties. These conditions are totally different in the case of free soot.

"Past Impingement Conditions. Many layers of carbon are deposited on the channel in succession. They are thus exposed to continued high temperatures and to the various gases present in the flame reaction. These factors are known to be capable of bringing about important differences in quality."

Possible improvements in processes.

Cabot (2) writing from his experience in 1912 says,

"I have personally no doubt that great economies are possible and would not for one minute wish to convey the impression that the Grantsville factory or any factory now in existence is the last word, but at the same time, they are the result of many hundreds of experiments by myself and others and we still peg away, trying every year to learn something and make some improvement and it is to me surprising that considering all the thought that has been given to the matter involved, so little progress has been made in the last twenty years."

Progress may go forward much more rapidly in the future. It is already possible by thermal decomposition to obtain from a hydrocarbon gas 30 to 40 per cent of the carbon. But because it is not understood how to control the factors that determine the quality, the carbon black produced by thermal decomposition

has little or no value.

Other methods, however, are being sought to increase the output without changing the quality. Francis (6) shows how the output of carbon black can be increased without changing the quality of the black by increasing the pressure of the flame. Other ways will be found either to raise the efficiency or to make better quality carbon black by existing methods.

Quality of carbon black.

The carbon black industry is one of the last to get from "the rule of thumb" method of testing. It was not until carbon black began to be used extensively in the rubber industry that a test was sought which could be repeated with any carbon black and its properties determined. It is possible that those who carry on experiments testing the quality of carbon black do not agree on the interpretation of the results (3) (16) (8) or that the structure of the carbon black with its adsorbed particles is yet not well enough understood to determine the characteristics of the black completely from physical tests. The fact that some progress is being made in determining the properties of a black, is encouraging. This is not being done for the rubber industry alone but also for other industries.

Kensley and Roberts (12) conclude:

1. Tinting strength is not an absolute function of the particle.

2. No direct ratio exists between tinting strength and tinting power.
3. The thickness of the film of adsorbed gases on the carbon black particles determines the tinting characteristics.
4. The volatile matter present and the oil-adsorption properties serve as a measure of the relative thickness of such films.
5. The completeness with which these gases are displaced materially affects the tinting strength.
6. Complete displacement is only possible when the interfacial tension produced by the dispersing medium at the surface of the carbon black particle is sufficiently low to assure complete wetting.

Adsorption.

In 1907 Davis (5) using iodine carried on a set of experiments to determine if adsorption is a surface or a solution phenomena.

At that time there were two schools, one headed by Travers (18) held that adsorption consists exclusively of a more or less complete adsorption into the interior of the solid, while the other school headed by Freundlich (7) asserted that adsorption is exclusively a condensation on the surface.

On the basis of his experiments with iodine adsorption

Davis stated, that he found that both surface condensation and diffusion into the interior of the solid phase would play an important part in cases of adsorption.

As evidence of the support of both theories Davis writes, "It was found in confirmation of the results of Freundlich that 'equilibrium' could be quickly attained from both sides. This must be due to purely surface action. Most striking confirmation of this view, and proof that a second factor comes into play, was obtained by observing the effect of long periods of time. It was found that for weeks and even months the carbon continued to adsorb the iodine, and this in relatively large quantities. These two facts can only be explained on the assumption that both surface action and diffusion into the interior of the carbon takes place. The surface condensation is nearly instantaneous; the formation of the solid solution is slower and requires weeks or months for its completion."

The next attempt at explaining adsorption was made by Langmuir (14) . Based on the results of his experiments with carbon filaments he says in part, "Judged from the great stability of this adsorbed layer, which enables it to be heated for half an hour at 2800° K. in the highest vacuum without being completely decomposed, a plausible guess as to its constitution is that it consists of oxygen atoms chemically combined with the carbon atoms which form the surface of the filament. According to our recent knowledge of the structure of solid

bodies, we have the best reasons for believing that the atoms of solid bodies are held together directly by chemical forces and that a crystal must be looked upon as a single molecule."

This belief of Langmuir was substantiated by his later experiments (13). While the theory is as yet not wholly accepted Johnson's (11) experimental work on the adsorbed gases in carbon black led him to believe, "that the same rule probably holds with respect to carbon black."

It is quite singular that so much information on a most puzzling physical question of adsorption should come from a source seemingly foreign to the subject. Langmuir got his idea of adsorption from the study of the filaments of tungsten and carbon in gases at low pressures. Becker (1) has not only shown that adsorbed particles exist as positive adions (adsorbed ions), negative adions or adatoms but he has pointed out the reason for the kind of adsorbed particle together with the ratios of the numbers existing and the length of time the particle will exist.

Whatever the mechanism is it is quite complex and involves forces that are not well understood. Lennard-Jones (15) has summarized the various existing theories of adsorption, and we might take as a working basis the surface phenomenon as adsorption, although it is well known that the experimental results of Davis were correct.

EXPERIMENTAL

Apparatus

The container.

The container in which the carbon was collected was a box made of asbestos slabs 12 inches square. The bottom of the container was made of bakelite as the asbestos allowed too much current to pass at the voltages used.

A 10 inch channel iron was fastened to the top slab of asbestos. A hole through the channel iron admitted the burner to the inside of the container from the top.

The burner.

The burner used was a lava tip of the rat tail 9 foot type; the same as those used in lamp black factories. The lava tip was fitted into an iron pipe drilled to make it fit snugly.

The position of the burner with respect to the channel iron was different from that used in carbon black factories. This was because of the electric field which was maintained between the channel iron and another electrode in the container. In order to keep the space between the two electrodes free, the

burner entered the container through a hole in the channel iron. It was arranged so that the lava tip came flush with the lower side of the channel iron. The flame, therefore, was directed downward, but would burn up against the channel iron. Only one burner was used.

Electric field.

For most of the experiments the channel iron formed the cathode and was connected directly to the center tap of a 220 to 100000 volt transformer on the 100000 volt side. The two ends of the secondary of the transformer were connected to earth through two kenotrons. In most of the work the ends of the secondary of the transformer winding were connected to the plate of the kenotron and the filament connected to the earth. The voltage to the transformer was supplied by a sine wave generator made by the General Electric Company. The voltage of the transformer was changed by changing the field of the generator.

The electric field in which the flame burnt was set up by means of the 10 inch channel iron 10.5 inches long and a copper plate 3 inches square and 1/16 inch thick. As previously stated the channel iron was connected to the center tap of the transformer. The copper plate was connected to the earth and formed the anode of the field.

For all the experiments, the cathode and anode were kept

aproximately parallel to each other and were separated from each other 5 inches.

The bakelite bottom of the container was used to prevent current leaking from the asbestos walls of the container to the anode.

Gas.

The gas used was the commercial gas sold by the Northwestern BlauGas Company. It is liquid at 80° F and at a pressure of 144 pounds per square inch. The volume of gas was measured by a standard wet test meter manufactured by the Precision Scientific Company of Chicago.

Method of Procedure

Commercial "propane" gas was burnt in a container approximately 1 cubic foot inside dimension. The air was admitted through a window in the front center of the container and the gas was allowed to escape through an opening in the top center opposite the front opening. The front opening was $2\frac{1}{4}$ inches by $\frac{5}{4}$ inch and the back opening was 2 inches by $\frac{7}{8}$ inch. This adjustment was made to give a sufficient amount of air to permit burning at all the possible voltages up to the voltage at which the arc formed between the anode and cathode. In some cases, however, the gas had to be ignited several times during

a run. This was done by means of a match held in the end of a glass tube.

Approximately one cubic foot of gas was burnt each time at 0.6 inch water tube pressure. The pressure was regulated by means of a pinch cock on a rubber tube and was kept constant throughout the run.

Collecting the carbon black.

At the end of the run the carbon black was collected as quickly as possible by brushing it from the channel iron and the sides of the container upon a piece of paper which had just been weighed. The paper and its contents were again weighed and the weight of the carbon taken to be the difference between the two weights.

The collection of the carbon black without loss is quite difficult under any condition. The problem becomes more difficult when one is trying to collect carbon black made under conditions that permit the particles to acquire a charge. It sometimes happened that considerable loss would result from approaching the carbon black particles with an object which carried an opposite charge. When an unusual loss was suffered the run was repeated.

The method of weighing the carbon immediately after it was made was decided upon after many trials of different methods to determine which would give the most consistent result.

This method was used only to determine the amount of black produced for each run. When a definite amount of black was required, such as in the tinting strength, the carbon black was dried and weighed on a watch glass.

Iodine adsorption test.

Iodine adsorptions were obtained by wetting 1 gram of black with 10 c.c. of glacial acetic acid, adding 25 c.c. of 0.0116 N. iodine solution, shaking mechanically for $2\frac{1}{2}$ hours, centrifuging, and titrating the residual iodine with thiosulfate solution 0.016 N.

This is approximately the method used by Palmer and Keller (17).

Tinting strength.

The tinting strength was obtained by mixing 0.05 grams of carbon black with 5 grams of zinc oxide and 75 drops of refined raw linseed oil. This was then mixed thoroughly and spread on a sheet of paper and allowed to thoroughly dry. Plates I to V show the samples as they were tested for coefficient of reflection.

These samples were tested with an automatic spectro-photometer for color analysis (25). The results are shown in Table I.

Each sample was analyzed for its reflection coefficient at various wave lengths of light from 4500 Angstrom units to 7000 Angstrom units, and from 0 volts to 22800 volts.

The electric current.

The electric current was measured by a galvanometer placed in the ground side of the circuit. The instrument was screened from electrostatic effects by completely surrounding it with an earthed copper screen. Readings were taken in both directions.

RESULTS

Effects of directing the gas downward.

When a hydrocarbon flame burns with the gas directed downward from a channel iron, the base of the flame, that is, the part at the channel iron will be broad and circular in shape. The flame from the base downward will have a funnel shape. Carbon black will collect on the channel iron in exactly the same way as it does when the flame burns below the channel and impinges against the channel iron. Comparison of the quantity of black made by the method described above with that obtained experimentally (17) shows only a small difference. The comparisons in tinting strengths and iodine adsorptions with standard commercial blacks show no greater variations than exist in commercial blacks made by similar processes. Any change, therefore, in quantity or quality of the carbon black cannot be attributed to the method of burning the gas against the channel iron by directing the flame downward instead of allowing it to impinge against the channel iron as it does in carbon black factories.

Changes due to the electric field.

The first noticeable effect of the electric field on the flame is the change in the shape of the flame. When the channel iron is the cathode, the flame seems to be drawn closer to it. There is, however, very little if any spreading of the flame. The volume seems actually to decrease. (Plate I and II). Accompanying this volume change is another very noticeable and exceedingly important change. It is the change in the way the carbon is deposited on the channel iron.

With no voltage between the channel iron and the copper plate, the carbon black is deposited in smooth layers of almost uniform thickness around the center of the flame, becoming thinner farther from the center. But at about 1600 volts (it is difficult to tell from observation just where the change begins) the carbon begins to be deposited in threads built downward from the channel iron. These threads of carbon black sometimes attain a length almost equal to the length of the flame. More will be said of this under the discussion of results.

As the voltage is increased these threads cease to form. The flame becomes smoky and dull. Carbon particles seem to be dispersed throughout the flame, and some of these particles escape from the container carried by the ventilating gases.

When the voltage has been increased sufficiently, (to about 3000 volts) this carbon dispersion ceases. The lower part of

the flame begins to appear blue like a flame that is well supplied with air but the base and one side remain yellow. With the appearance of the blue, the flame seems to become longer as though it were reaching out to the anode. That, really, is what it is doing for when a discharge takes place between the cathode and the anode the flame is mostly blue. It frequently happens that the flame is carried with the electrical discharge away from the cathode to the anode and becomes extinguished. When this happens, the major part of the flame is always blue, and it happens, in general, more frequently with higher voltages. This, however, is not always true but the factors which cause it to deviate from the above rule have not been determined. It has been observed that on different days the flame could be made to burn with much higher voltages between the electrodes than on other days. At this time, however, no significant correlation has been made between this phenomena and atmospheric pressure or humidity.

At any voltage which causes a relatively large portion of the flame to be blue, the carbon black deposited has a different figure. Instead of the carbon threads forming down from the iron as they did at lower voltages, they built radially out from the center of the flame with very irregular layers. The whole figure resembles very much in appearance the Lichtenberg figures for negative voltages.

All the carbon black does not remain on the channel iron.

It coagulates into larger particles very much resembling soot. A carbon black particle seems always to have a positive charge but these larger particles are quite likely to have a negative charge induced upon them. When this happens the soot particle is forcefully driven away from the negative plate. If the particle happens to be directed toward the positive plate, it will strike there and may or may not acquire a positive charge sufficient to drive it away from the positive plate. As the voltage increases the quantity of these coagulated soot particles increases. They are driven by electrostatic forces to all parts of the container.

There is always a voltage at which the flame cannot be kept burning. When this voltage is approached the flame becomes mostly blue and acts very much as if there is a deficiency of oxygen. It has been observed, however, that the flame burns better when the channel iron has a coat of carbon black on it. This might be due to the better heat insulation furnished by the carbon black.

Temperature of the channel iron.

The temperature of the channel iron was obtained by keeping a thermometer in a hole drilled entirely through the iron about 2 inches from the burner. Readings were taken at intervals, but they are quite likely not thoroughly reliable because the carbon black deposited on the channel iron was a

very good heat insulator. The decrease in the temperature of the channel iron is due to the increasing thickness of this carbon black deposited on the plate. In general the temperature was lower for the higher voltages.

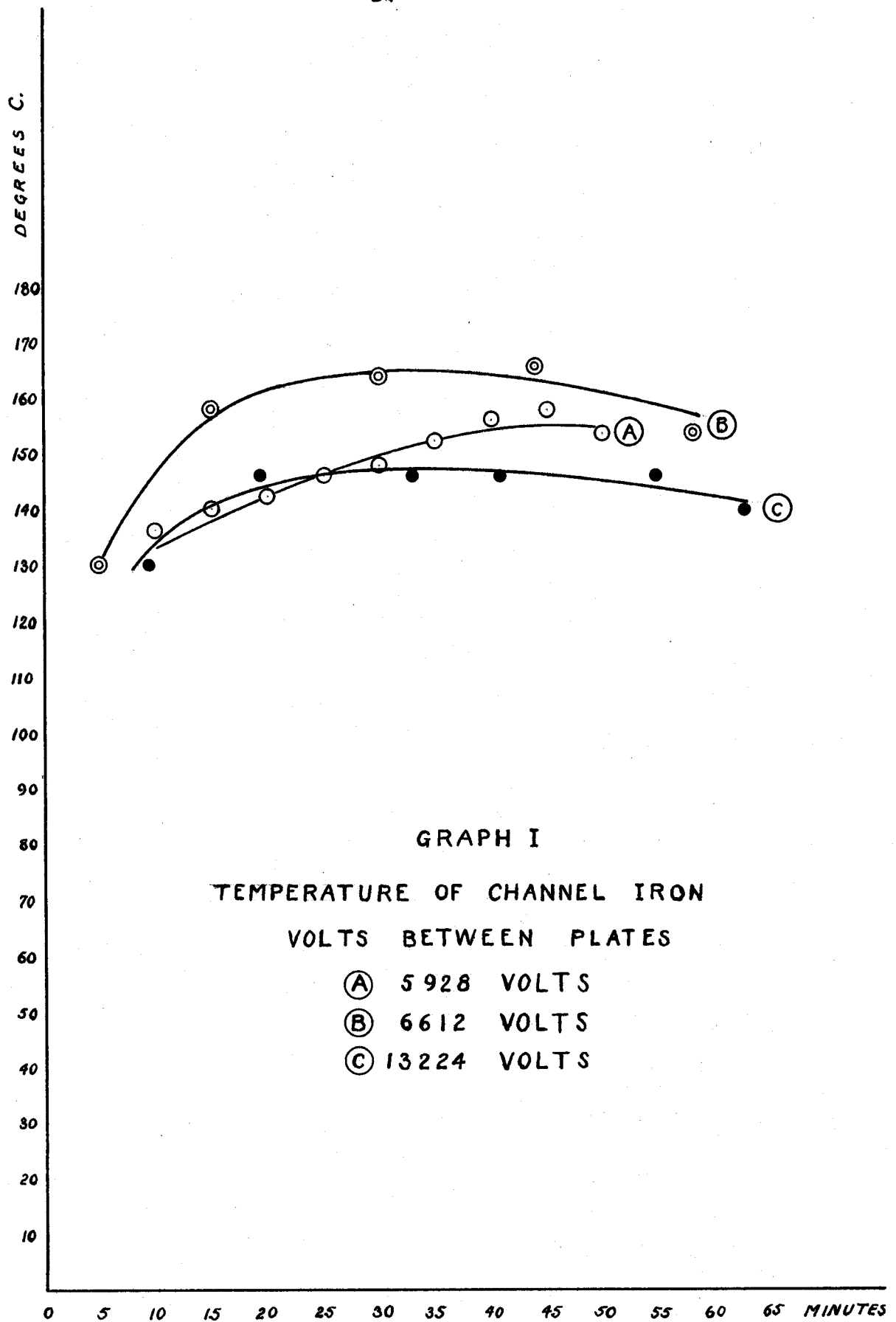


Plate I



Flames burning from glass tubes showing the halo around the flame. No voltage applied.

Plate II



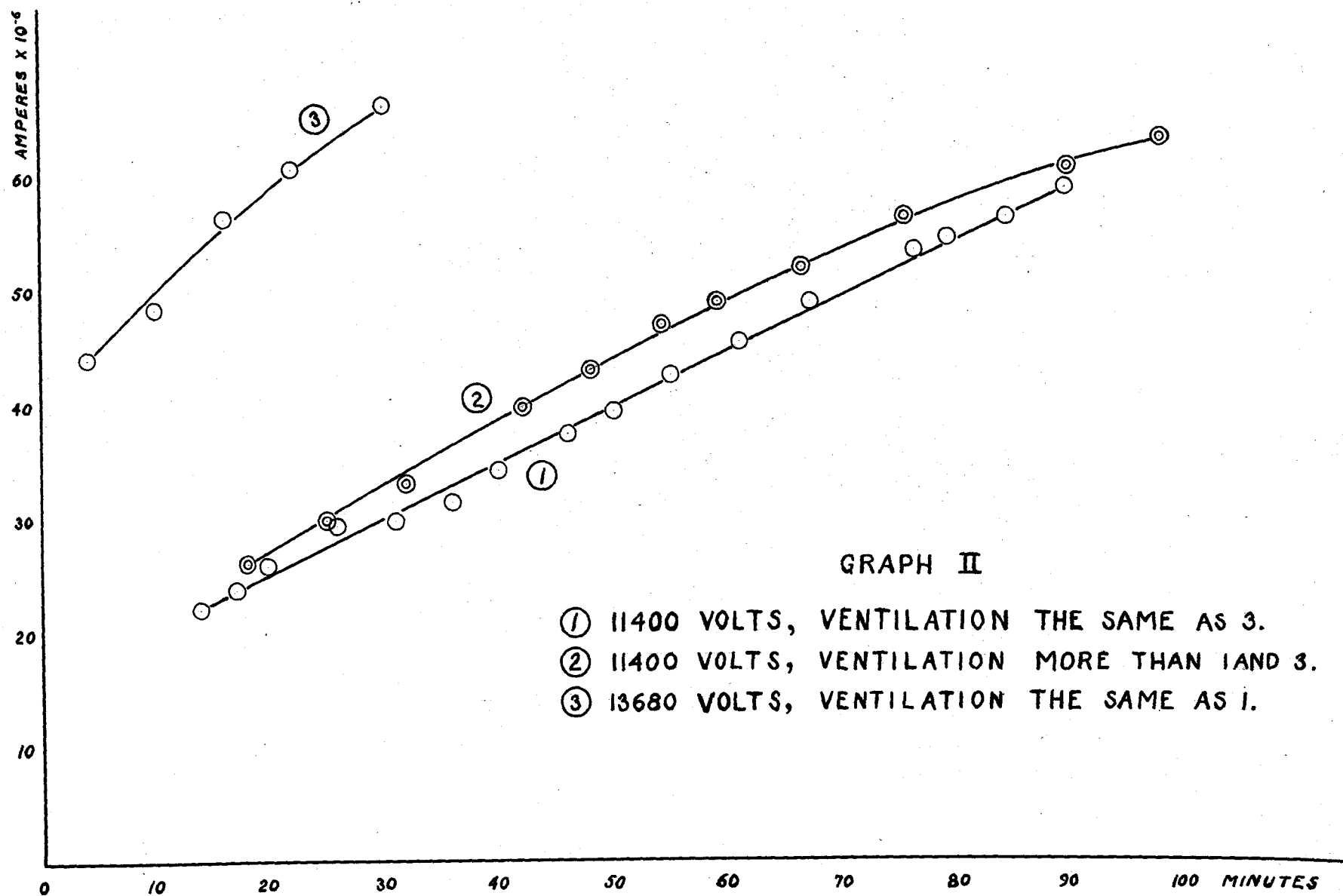
-26-

The same flames as in Plate I showing the increase in the halo around the $+$ flame and a decrease around the $-$ flame with voltage applied.

Variation of current with time.

There exists rather a complex current time relation. Three of these curves are shown on Graph II. The two which are shown for 11400 volts illustrate the variation of current with constant voltage but with different amounts of ventilation. Curve 2, which is the one for the condition when more air was admitted than for 1, shows a greater current throughout. There was also a greater amount of carbon deposited for the run shown by Curve 2, the ratio being 1.50/0.52. Curve 3 shows the current to the same scale for 13680 volts.

It appears from these data that the current increases with the amount of carbon on the channel iron. If that be true, the rate at which carbon was deposited was almost constant throughout each run.



Variation of the quantity of carbon black with electric field.

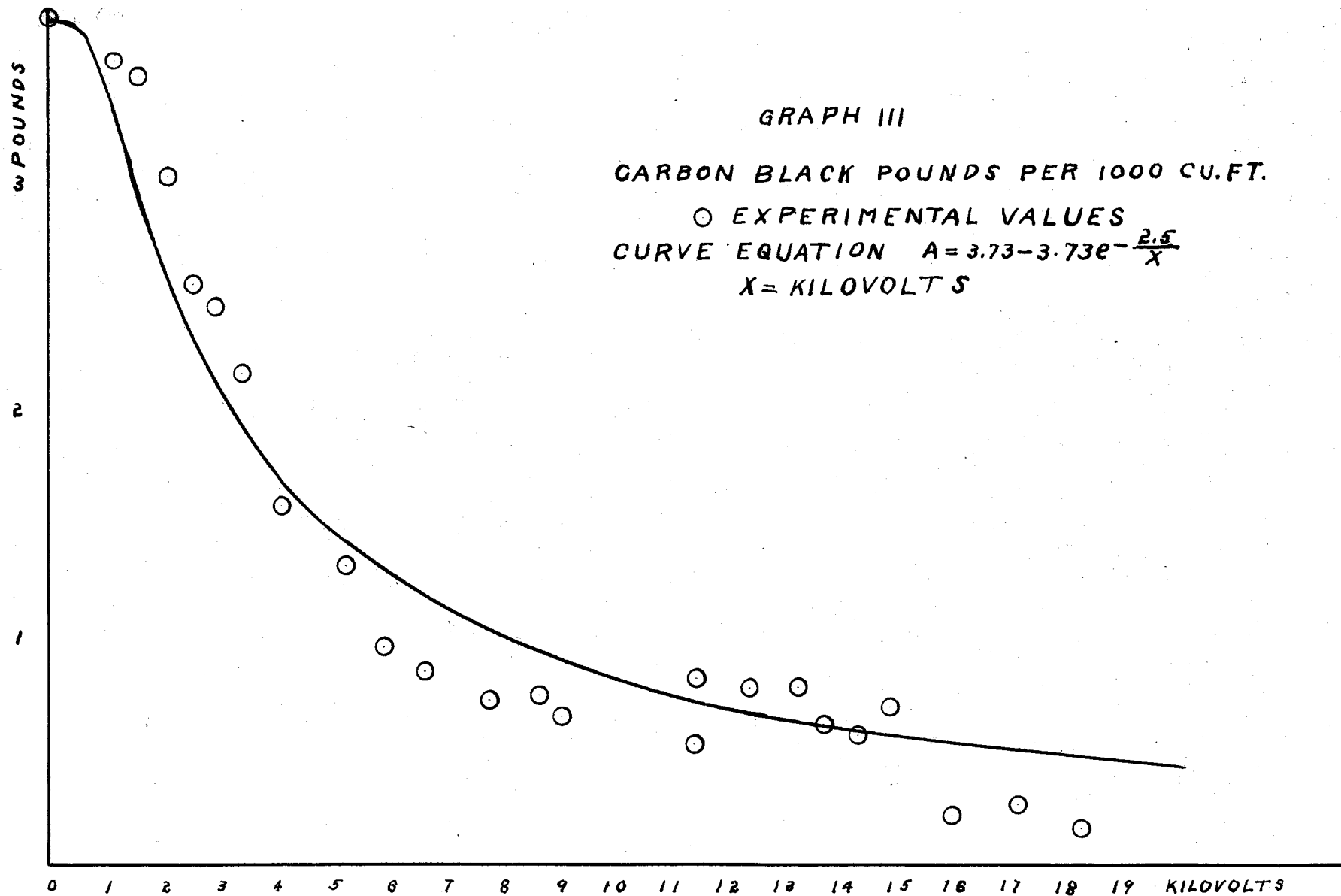
When no change is made in the conditions of burning but the change in field strength, the quantity of carbon black deposited will change. The way these two quantities vary with each other is shown in Graph III and Table I.

There are three factors, in the relation between the field strength and quantity of carbon black, that are important.

1. The curve from 0 to 1000 volts has a decreasing slope. Above 1000 volts, the curve has an increasing slope.
2. From 1000 volts on the carbon black voltage relation follows a definite mathematical law.
3. The experimental relation always ends by the flame being extinguished.

Table I

Volts between electrodes	Time in minutes	Carbon black lbs/1000 cu. ft. calculated	Carbon black grams per cu. ft. measured	Maximum Temperature of channel iron. C
00	105	3.75	1.710	---
1140	110	3.51	1.594	---
1596	95	3.46	1.570	---
2052	100	3.17	1.444	---
2508	110	2.53	1.146	---
2964	110	2.43	1.101	---
3420	105	2.15	0.858	---
4104	107	1.57	0.712	---
5244	105	1.35	0.614	---
5928	100	0.95	0.431	158
6612	94	0.83	0.376	166
7752	105	0.71	0.324	166
8664	119	0.74	0.339	164
9032	110	0.65	0.293	155
11400	100	0.51	0.235	150
12312	105	0.77	0.350	156
13224	105	0.77	0.350	146
13680	108	0.65	0.294	---
14250	100	0.55	0.251	154
15960	100	0.21	0.096	154
18240	95	0.14	0.066	158



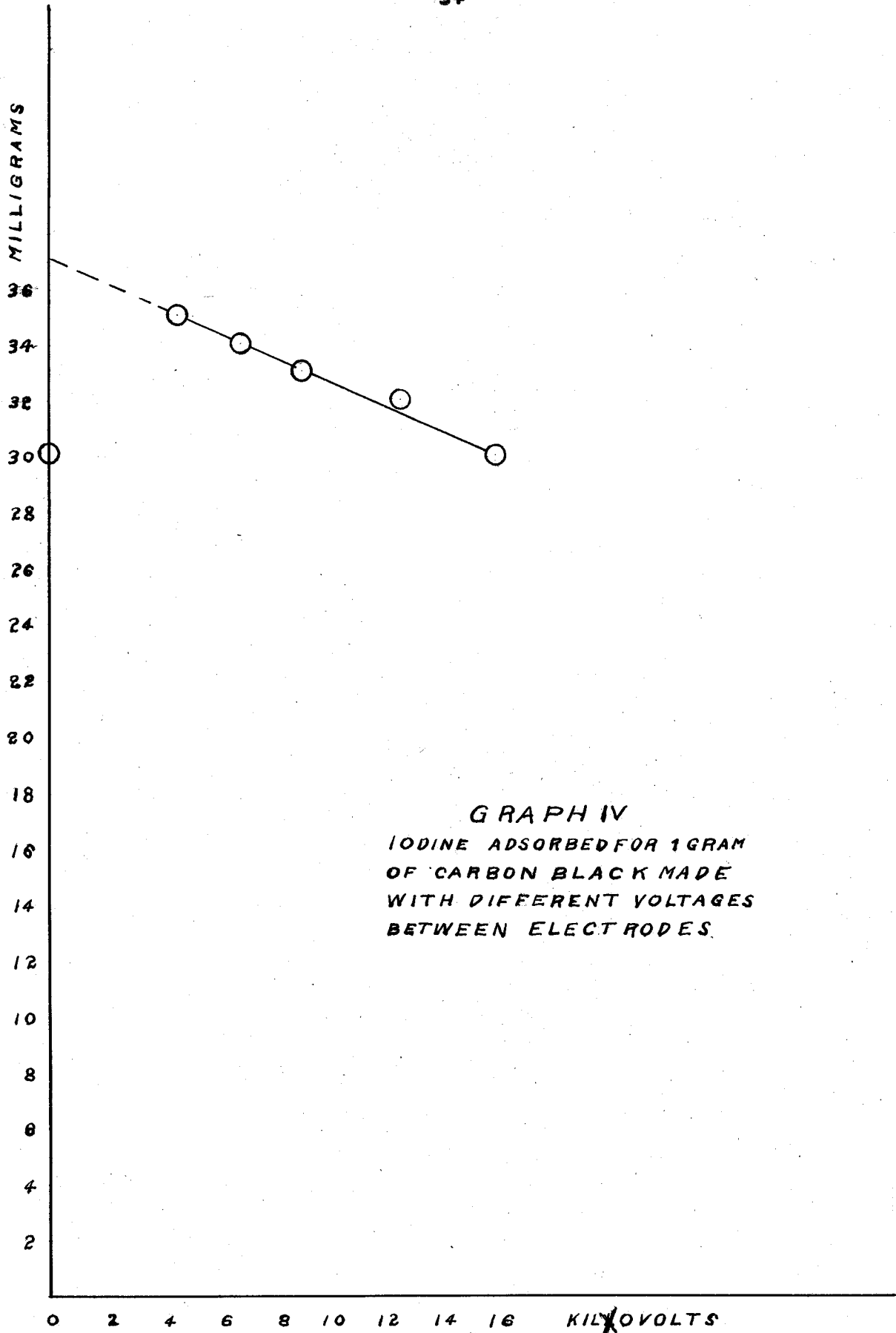
Iodine adsorptions and tinting strength.

The relation between the iodine adsorptions and field strengths, presented in Table II and Graph IV, shows a straight line variation. As the voltage increases the adsorption becomes less. This seems to indicate a decrease in the amount of surface exposed for a given amount of carbon black. The carbon particles, therefore, are larger. There seems to be no very definite relation between the adsorption of the carbon black made at zero voltage, and the adsorptions of the carbon blacks made with voltages. Enough data are not available to determine this.

The data in Table III give the coefficient of reflection for samples made with 0.05 grams of carbon black, 5.00 grams of zinc oxide and 75 drops of linseed oil. There seems to be some rather definite governing factor between voltage and tinting strength but it is not clear from the data what this is. As is the case with iodine adsorption no relation has been found between the carbon black made at no voltage and that made with voltage.

Table II

Volts	: Iodine adsorption : in grams : per gram of black
0000	: 0.0301
4560	: 0.0358
6840	: 0.0344
9120	: 0.0336
12540	: 0.0327
15960	: 0.0300



GRAPH IV
IODINE ADSORBED FOR 1 GRAM
OF CARBON BLACK MADE
WITH DIFFERENT VOLTAGES
BETWEEN ELECTRODES

Table III

Reflection Factor at Various Wave Lengths \AA .

Volts	: 4500	: 5000	: 5500	: 6000	: 6500	: 7000
Multiply by 228:	R.F.	R.F.	R.F.	R.F.	R.F.	R.F.
Standard black:	.0979	.0948	.0927	.0842	.0834	.0816
0 volts	.1070	.0990	.0969	.0926	.0875	.0857
10 volts	.1280	.1205	.1178	.1125	.1107	.1050
20 volts	.1245	.1166	.1150	.1090	.1070	.1030
30 volts	.1190	.1119	.1095	.1000	.1005	.0970
50 volts	.1235	.1184	.1159	.1083	.1065	.1010
60 volts	.1259	.1205	.1179	.1125	.1106	.1050
80 volts	.1281	.1205	.1179	.1165	.1127	.1090
*91 volts	.1256	.1183	.1156	.1115	.1083	.1061
*100 volts	.1230	.1145	.1106	.1050	.1050	.1041

*The values of these readings are doubtful. The flames were put out so many times by the voltages that the carbon black deposited when the voltage was not on could easily affect the results shown.

Plate III



0.05 grams of Cabot's Stirling carbon black.

5.00 grams zinc oxide.

75 drops raw linseed oil.



0.05 grams of carbon black made with 6 volts between electrodes.

5.00 grams of zinc oxide.

75 drops of raw linseed oil.

Plate IV



0.05 grams of carbon blacks made with
2280 volts between electrodes.

5.00 grams zinc oxide.

75 drops raw linseed oil.



0.05 grams carbon black made with
4560 volts between electrodes.

5.00 grams of zinc oxide.

75 drops of raw linseed oil.

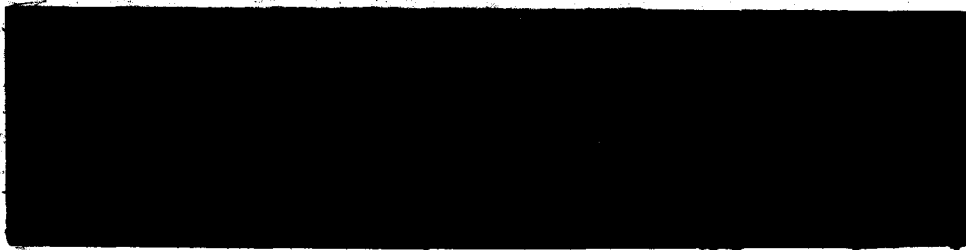
Plate V



0.05 grams of carbon black made with
6840 volts between electrodes.

5.00 grams zinc oxide.

75 drops raw linseed oil.



0.05 grams of carbon black made with
11400 volts between electrodes.

5.00 grams zinc oxide.

75 drops of raw linseed oil.

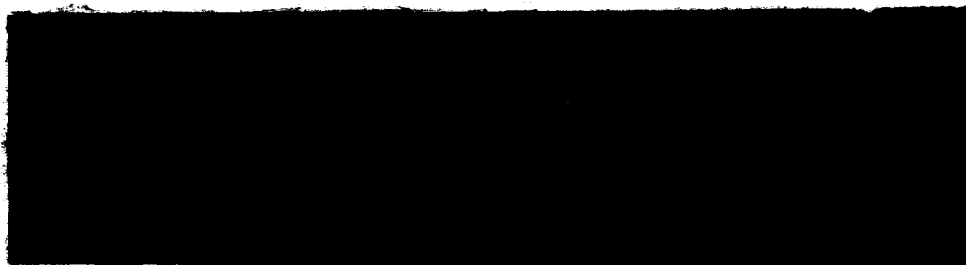
Plate VI



0.05 grams of carbon black made with 13680
volts between electrodes.

5.00 grams zinc oxide.

75 drops of raw linseed oil.



0.05 grams of carbon black made with 18240
volts between electrodes.

5.00 grams of zinc oxide.

75 drops raw linseed oil.

Plate VII



0.05 grams carbon black made with
20860 volts between electrodes.

5.00 grams zinc oxide.

75 drops raw linseed oil.



0.05 grams carbon black made with
22800 volts between electrodes.

5.00 grams zinc oxide.

75 drops raw linseed oil.

DISCUSSION OF RESULTS

Relation between strength of electric field and quantity of carbon black.

The curve in Figure 1 shows the relation between the intensity of the electric field and the amount of carbon deposited for a given ventilation. If the amount of air admitted to the container is increased the production of carbon is increased. Of course, there is an upper limit to this for eventually the oxygen admitted would enter into chemical combination with the carbon to such an extent that the carbon black deposited would decrease.

The fact that an increase of air, over the amount necessary to support combustion, gives an increase in the amount of carbon black is important. In the first place it shows that the decrease in amount of carbon black with increased potential is not due to an increased amount of ozone. Secondly it shows that air is absolutely essential for the production of carbon black.

If the increased oxidizing properties of the gas caused by the ozone were responsible for the decrease in carbon black for increase of potential, combustion would be more active with any increase of potential, but this is not the case. The flame

becomes dull and less active. The temperature of the channel iron never was as great with the higher voltages as it was with no voltage even though the rate of flow of gas was the same. If ozone were the cause of the decrease of carbon black with increase of voltage, when more oxygen is admitted there would be more ozone and consequently less carbon black, but as already stated an increased supply of air gives more carbon black.

The fact that additional air gives an increased supply of carbon black, is sufficient evidence that air is quite essential to the production of carbon black. It is reasonable to suppose that it is the oxygen that plays the important role. There is in the container an abundant supply of all the other gases. If nitrogen for example were the essential gas to cause the formation of carbon black there is a sufficient amount present under any condition of combustion to form the carbon black. Carbon dioxide and carbon monoxide are also present in a sufficient quantity. The fact that the amount of oxygen is small in comparison to the amount of carbon dioxide and carbon monoxide (22) in the analysis of the gas given off at 445° C. is no evidence that it is these gases which are adsorbed. Langmuir (14) found that it was impossible to remove free oxygen from a carbon filament but that it always came off as CO_2 or CO . The oxygen persisted on the carbon filament even at temperatures as high as 2200° K. and in the highest

vacuum. The oxygen could be removed from a tungsten filament much more readily. He concluded that the forces which bind the carbon to the oxygen are much greater than the forces which bind the oxygen to tungsten and that they must be chemical in nature.

From the analysis of carbon black given by Perrott (22), for long black the ratio of the oxygen atom to the carbon atoms is about 1:17 while for the short black this ratio is about 1:51 or three times as many carbon atoms for each oxygen atom in the short black as in the long black.

Johnson (10), found a very definite relation between the volatile matter in carbon black and the quality imparted to vulcanized rubber. Carson and Sebrell (3) think the amount of volatile combustible matter is a measure of the quality of the black for use in rubber. They feel however, that it would be difficult to use on account of the slight variation in amounts necessary to give quite different properties to the rubber. They consider a better test is the ability of the carbon black to remain in suspension. Kensley and Roberts (12) found that the thickness of the film of adsorbed gases on the carbon black particles determined the tinting strength. All these observers have found that the property of the black is in some way very definitely related to the gas with which the carbon is associated.

Carbon obtained from natural gas by cracking processes has very little if any use as carbon black. Analysis shows that carbon obtained in this way has but little oxygen content (22).

This all supports the belief that oxygen plays a very definite part not only in the uses of carbon black but in its formation. What then is the mechanism of the formation of carbon black?

The process by which carbon black is made is to burn gas and allow it to impinge against a surface usually iron although soapstone was originally used with no noticeable effect when iron was substituted (2). By a series of reactions in the flame, quite likely both chemical and physical, carbon black is produced. Bone and Townend summing up the discussion on the cause of the luminosities of hydrocarbon flames say, "While most authorities will probably agree that the separation of finely divided carbon in the thermal decompositions of such hydrocarbons is in all probability a potential cause of the luminosity of their flames, it needs to be emphasized that, with the possible exception of acetylene, their rates of decomposition are far slower than those of their combustion at the temperatures prevailing in flames. This fact coupled with their undoubted great affinity for oxygen, impels us to the conclusion that in the propagation of a flame through a homogeneous mixture of hydrocarbon and oxygen (air), oxidation

will probably take precedence of all other chemical phenomena. Hence in such cases we must also look to the thermal decomposition of hydroxylated molecules and aldehydes (but not formaldehyde) as at least a contributory, if not the main, cause of carbon deposition." Here is summed up the chemical view of the action in a flame. If the combustion is complete the result is CO and CO₂. The intermediate steps from the initial point to the completion of combustion of a hydrocarbon gas are complex and difficult to measure. Various theories and chemical equations have been advanced to explain the intermediate steps for both complete and incomplete combustion. The incomplete combustion always giving free carbon as one of the final products. Various reasons have been given for the freely divided state of this carbon. One of the easiest to think of and consequently most often advanced is; if the flame is allowed to impinge on a surface the particle does not have time to agglomerate with other carbon particles. The high temperature was thought necessary to large particle size and consequently gritty carbon.

The idea of removing the carbon from the flame quickly or keeping the flame cool can be seen carried out in the design of equipment of plants. One such plant was built in about 1902 with hollow channels through which gas was blown (22). The process has been abandoned. The electric field was used experimentally to remove the positively charged carbon particles

from the flame quickly. This already has been referred to.

It has long been known that carbon black of any kind contains adsorbed gases and chief among these is oxygen. The gases however have been thought to be adsorbed on the carbon particles and apparently until recently little or no attention has been paid as to how or when these gases were adsorbed. Langmuir during his work with the carbon filament came to the conclusion that the oxygen atoms were held in chemical combination with the carbon atoms. How this chemical combination is made or what is the strength of the bond is not stated but as has already been said this bond is sufficiently strong to prevent the oxygen being removed from the carbon atom by physical means. Carbon produced by cracking methane shows no such tendencies to adsorb oxygen as do other carbon blacks. Chemical analysis which shows long carbon black to contain eight per cent oxygen shows that the carbon obtained from cracking methane contains only a fraction of one per cent oxygen (22), and that produced by cracking natural gas, no oxygen at all. Of course, it is quite possible that the small amount of oxygen adsorbed by the carbon produced by the cracking process would not show in chemical analysis. This, however, will not account for the large amount adsorbed by carbon black. How then can the adsorbed oxygen be accounted for?

Carbon black due to reaction in the flame.

The data which show the relation between the strength of the electric field and the quantity of black deposited are significant. Let it be assumed that oxygen is essential for the production of carbon black, and that this oxygen must be in the flame at the time the carbon black is formed. Also let it be assumed that the amount of carbon black formed is directly proportional to the combinations between these carbon and oxygen atoms, and that these combinations are due to collisions. Now since the gases all about the flame are ionized it is certain that the gases in the flame are also ionized. It is equally certain that both positive and negative ions exist in the flame (24). Let the relative mobility of these ions be K , and suppose that when one negative ion strikes a positive ion the chance of their uniting to form a carbon black particle is $\frac{1}{n}$ where n is the number of collisions an ion must make before it forms a carbon black particle. Now if the strength of the electric field is X , the relative velocity of drift of the ions will be KX . Suppose this velocity to be small compared to the velocity V due to thermal agitation.

With these assumptions we can follow the method of mathematical development due to Thomson (24) to show the combinations to produce carbon black particles in the flame.

To calculate the chance of an ion passing over the distance

x parallel to the electric field without becoming attached to an ion of opposite sign, proceed as follows: The time taken to pass over the distance x is $\frac{x}{KX}$ and in this time the length of the path described by the ion is $\frac{Vx}{KX}$ where V is large compared to KX . Let $\alpha = \frac{V}{KX}$ then this distance will be αx .

By the kinetic theory of gases the expectation of the ion traveling this distance without a collision is $e^{-\frac{\alpha x}{\lambda}}$ where λ is the mean free path of the ion; this is also the expectation that it should travel over this distance without making a collision.

The chance that it makes one collision and no more in passing over a distance x may be found as follows: the chance that it makes a collision between y and $y + dy$ is $\frac{\alpha dy}{\lambda}$, the chance that it does not make a collision during the rest of the journey is $e^{-\frac{\alpha(x-y)}{\lambda}}$ hence the chance that a collision should occur between y and $y + dy$ and that this should be the only one is

$$\frac{\alpha dy}{\lambda} e^{-\frac{\alpha y}{\lambda}} e^{-\frac{\alpha(x-y)}{\lambda}} = e^{-\frac{\alpha x}{\lambda}} \frac{\alpha}{\lambda} dy$$

The chance that it should make one, and only one collision in a distance x is, therefore

$$\int_0^x e^{-\frac{\alpha y}{\lambda}} \frac{\alpha}{\lambda} dy = e^{-\frac{\alpha x}{\lambda}} \frac{\alpha x}{\lambda}$$

The chance that this collision does not result in a carbon black particle is $1 - \frac{1}{n}$, the expectation of the ion getting across with one collision is

$$e^{-\frac{\alpha x}{\lambda}} \cdot \frac{n-1}{n} \cdot \frac{\alpha x}{\lambda}$$

The chance that the ion makes just two collisions in its journey is

$$\int_0^x e^{-\frac{\alpha y}{\lambda}} \cdot \frac{\alpha y}{\lambda} \cdot e^{-\frac{\alpha(x-y)}{\lambda}} \cdot \frac{\alpha}{\lambda} dy$$

for $\frac{\alpha dy}{\lambda}$ is the chance that it makes a collision between y and $y+dy$, $e^{-\frac{\alpha y}{\lambda}} \cdot \frac{\alpha y}{\lambda}$ is the chance that it makes one collision and no more before reaching y , and $e^{-\frac{\alpha(x-y)}{\lambda}}$ is the chance that it makes the rest of the journey without a collision. The value of the integral is

$$e^{-\frac{\alpha x}{\lambda}} \cdot \frac{1}{2} \left(\frac{\alpha x}{\lambda} \right)^2$$

the chance that neither collision should result in a carbon black particle is

$$\left(\frac{n-1}{n} \right)^2$$

The expectation of a two collision ion crossing in a free state is

$$e^{-\frac{\alpha x}{\lambda}} \cdot \frac{1}{2} \left(\frac{n-1}{n} \cdot \frac{\alpha x}{\lambda} \right)^2$$

Similarly the expectation of a three collision ion crossing in a free state is

$$e^{-\frac{\alpha x}{\lambda}} \frac{1}{2 \cdot 3} \left(\frac{n-1}{n} \frac{\alpha x}{\lambda} \right)^3$$

and so on. Since all the ions must make an integral number of collisions between zero and infinity, the expectation of an ion crossing in the free state is

$$\begin{aligned} e^{-\frac{\alpha x}{\lambda}} \left\{ 1 + \frac{n-1}{n} \frac{\alpha x}{\lambda} + \frac{1}{2} \left(\frac{n-1}{n} \frac{\alpha x}{\lambda} \right)^2 + \frac{1}{2 \cdot 3} \left(\frac{n-1}{n} \frac{\alpha x}{\lambda} \right)^3 + \dots \right\} \\ = e^{-\frac{\alpha x}{\lambda}} e^{(n-1) \frac{\alpha x}{n \lambda}} \\ = e^{-\frac{\alpha x}{n \lambda}} \end{aligned}$$

If N ions react to form carbon black particles when no electric field exists between the plates the number which will be drawn out of the flame before carbon black particles are formed is

$$N e^{-\frac{\alpha d}{n \lambda}}$$

where $x = d$ the distance from $x = 0$ to the end of the flame. The number of ions left in the flame to form carbon black will be

$$A = N - N e^{-\frac{\alpha d}{n \lambda}} \quad (1)$$

If n , d , V and K remain constant this equation becomes

$$A = N(1 - e^{-\frac{c}{x}}) \quad (2)$$

The curve on page 31, Graph III, is plotted from equation 2, page 51. The points on Graph III show the experimental determinations of the quantity of carbon black for various values of voltages. The very close relation between the experimental values and the theoretical values shows definitely that the equation is derived from correct assumptions.

The formation of carbon black, therefore, must be due to collisions between ions in the flame.

The points on the voltage quantity curve Graph III, show very clearly the relation between the experimental results as shown by the points and the curve plotted from equation (2).

It is quite difficult to understand how an oxygen atom can hold more than a hundred carbon atoms in combination to form a carbon black particle, but if the analysis of carbon black shows the oxygen that entered into combination with it when it was formed and from which it cannot be separated, that is what we have to conclude.

The flame.

It is now quite easy to see why a flame will not burn in a strong electric field. When the field is made strong enough to separate the ions they cannot enter into any combination not even the ordinary chemical one.

The flame looked at from this viewpoint takes on a new meaning. Its boundaries form a container in which the interior gases are ionized, mixed and enter into chemical combinations. The flame is to gases what the solution is to solids. It is where partly chemical and partly physical phenomena take place.

Iodine adsorption.

The carbon black iodine adsorption was tested with the results shown in Figure 2. The straight line characteristic between iodine adsorption and voltage would seem to indicate

that the carbon atoms in the electric field are polar. What is likely is that the molecule in which the carbon atom is held just before forming carbon black, is polar. The electric field causes these polar molecules to line up in such a way as to bring a number of the carbon atoms together in the same way a crystal is formed from a solution. When there is a collision between two such molecules in such a way as to cause the carbon atoms to unite there is formed in this way a small carbon crystal with every carbon black particle. The size of these carbon crystals increases with the field strength. That is, in every carbon black particle made with an increasing field there are more of the carbon atoms joined together in this way thus presenting a smaller surface for a given weight of carbon black. This smaller surface adsorbs less iodine. It is quite likely that some of these particles reach their final dimensions without having even united with an oxygen atom. This however is not known since the volatile matter of the carbon black was not tested. If the above assumption is correct, it would follow that iodine adsorption would be no test of the quality of carbon black as it would only determine the ratio of the surface exposed and in no way would it be related to the volatile matter. This is shown by tests (3).

It seems quite likely that the quality of carbon black made by different processes depends to a large extent on the electric potential at the surface of the iron against which the carbon black is formed.

Tinting strength.

The tinting characteristic of carbon black according to Kensley and Roberts (12) is determined by the thickness of the adsorbed gas film. According to the latest views on adsorption (5a) at surfaces it is doubtful if an adsorbed gas can be more than a molecule thick on a surface.

The tinting strength shows very little variation with voltage. This is illustrated in Table III which gives the coefficient of reflections from the plates III to VII. There is however quite a large difference between the color reflection of the plate made without voltage and those made with voltage. From the number of samples made and the relative wide range of voltages covered it is doubtful if the data have any great significance. It is presented here, however, because it shows a new and very powerful means of detecting the difference in color of the various samples.

This method of measuring the relative reflection coefficients of different carbon black zinc oxide mixtures should prove a very powerful tool. A pure white gives a definite quantitative standard to which the tinting strength of any carbon black can be compared by comparing the light reflected by the sample to that reflected by the standard.

It should be observed from the samples shown that very little difference can be detected by the eye in their color. The

analysis however shows quite a decided difference even with the small amount of data shown.

CONCLUSIONS

The experimental results prove the following:

1. For a given amount of gas and ventilation, the quantity of carbon black varies with the amount of voltage between the electrodes.

2. The variation may be shown by the method of mathematical development due to Thomson to be according to the law

$$A = N(1 - e^{-\frac{C}{X}})$$

where A = the amount of carbon black formed

N = the carbon black formed with no voltage

C = a constant

X = voltage between electrodes

3. Since the experimental data are in accord with the law given in (2), carbon black is formed as the result of a collision between an ion and the carbon atom or carbon ion.

4. The iodine adsorption varies with the voltage at which the carbon black is made. This relation is shown in Graph IV, and indicates a decrease in surface for a given weight of carbon black.

5. There is a relation between the tinting strength of carbon black and the voltage at which the carbon black is made. This is shown by table III.

6. Plates III to VII shown in the data to illustrate

the variation in tinting strengths of carbon black, prove very definitely the value of the automatic spectra photometer, which was here first used for this purpose. The principal advantages it has over simple comparison methods previously used are:

a. It gives a definite standard (white) to which all samples can be compared.

b. It detects a very slight difference in color at different wave lengths.

7. Since carbon black is the product of a union between an ion, probably oxygen, and a carbon molecule or carbon ion and as this union is made in the flame under ionized conditions, carbon black can be made by thermal decomposition (cracking) of natural gas, and the grade of carbon black controlled.

8. It appears from observations made of the flame and the carbon black deposited, that combustion is not wholly a thermal reaction but depends on the electrostatic condition surrounding the flame.

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